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Optical Characterization of novel photocrosslinkable second-order nonlinear optical (NLO) polymers are presented. These polymer systems have been designed with nonlinear optical moieties in the polymer main chain. When poled and sufficiently photocrosslinked, these polymers exhibit relatively stable second-order nonlinearity at room temperature. The linear optical and second order NLO properties of these recently synthesized polymers have been investigated. Second harmonic generation (SHG) was utilized to monitor the temporal stability of the nonlinearity. The linear electro-optic coefficients were measured with a modified Michelson interferometer.

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Stable Second-Order Optical Nonlinearity
in Novel Photocrosslinkable Polymers

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ABSTRACT

Optical characterization of novel photocrosslinkable second-order nonlinear optical (NLO) polymers are presented. These polymer systems have been designed with nonlinear optical moieties in the polymer main chain. When poled and sufficiently photocrosslinked, these polymers exhibit relatively stable second-order optical nonlinearity at room temperature. The linear optical and second-order NLO properties of these recently synthesized polymers have been investigated. Second harmonic generation (SHG) was utilized to monitor the temporal stability of the nonlinearity. The linear electro-optic coefficients were measured with a modified Michelson interferometer.

1. INTRODUCTION

Recently nonlinear optical (NLO) polymeric materials have attracted considerable attention for applications such as fast electro-optic modulation and waveguide frequency doubling.[1] These materials possess large second-order NLO coefficients when poled, and the optical and other physical properties can be easily tailored by either doping or covalently incorporating different functional groups into the polymer matrices. The polymeric materials can be spun into good optical quality thin films and laborious crystal growth steps are eliminated.

Unfortunately, the electric field induced polar orientation of dipolar NLO moieties in the amorphous polymer slowly randomizes due to thermal motion of the polymer chain and NLO chromophore. This results in a slow decay of second-order NLO properties at room temperature in times ranging from a few months to about a year. The stability of the second-order nonlinearity of the poled polymer is an important issue that still needs to be

addressed. Earlier a thermally cross-linkable epoxy system showing stable NLO response at room temperature was reported by Eich *et al.*[2] Recently, we have utilized photocrosslinking technique to achieve stable NLO property in a poled guest-host polymer, where crosslinking of the aligned dipolar NLO molecules was performed by irradiating the sample with UV light during the late phase of poling.[3,4] These polymers are processed in a manner similar to a doped polymer system except photocrosslinking groups are attached to the guest NLO molecules as well as to the host polymer. It was shown that these polymers can be directly patterned by shining UV light through a mask for making channel waveguides and other integrated optical devices.[5] More recently, photocrosslinkable polymers with NLO moieties incorporated in the polymer main chains have been synthesized.[6] This paper reports on optical properties of members of one class of these new main chain polymer systems.

2. MATERIAL PREPARATION

The chemical structures of the four polymers investigated are shown in Fig.1, where they have been named as 40, 43, 50 and 53. The detailed synthesis of these polymers were reported in ref. 6. These polymers were designed with nitroaniline type NLO chromophores. Polymers 40 and 43 were functionalized with photoreactive cinnamoyl groups. Polymers 50 and 53 contain a styrylacryloyl group as the photocrosslinking group instead of the cinnamoyl group. This makes these polymers sensitive to violet and near-UV for photocrosslinking. The polymer films were prepared by spin coating solutions of these polymers in propylene glycol methyl ether acetate (PGMEA). These films were placed in a vacuum oven at room temperature for 12 hours and then baked at 40 °C for another 12 hours to remove residual solvent. Typical film thickness obtained were about 0.5 μm. The glass transition temperatures T_g of these polymers were measured with a differential scanning calorimeter (DSC) in the uncrosslinked state to be 83.4 °C for polymer 40, 78.2 °C for polymer 43, 84.6 °C for polymer 50 and 88.0 °C for polymer 53. The refractive indices were measured with an ellipsometer. The absorption characteristics were obtained with a UV-visible-NIR spectrophotometer. These polymers are transparent in visible and near-IR frequency regime. The measured absorption peak wavelengths of the NLO chromophores and all the other measured results on these novel polymers are summarized in Table I. In the case of polymers 50 and 53, the NLO chromophore absorption peaks are overlapped by those of the photoreactive groups (around 370 nm).
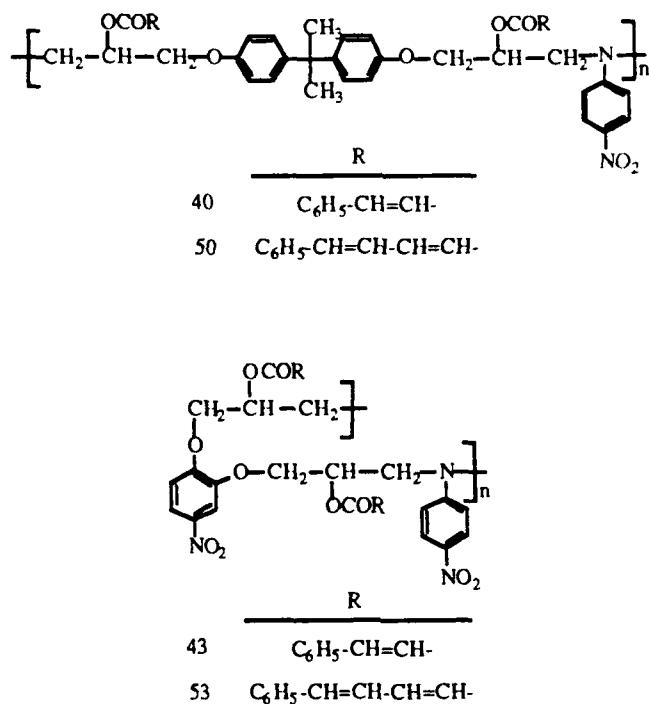
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	R
40	C_6H_5-CH=CH-
50	C_6H_5-CH=CH-CH=CH-

	R
43	C_6H_5-CH=CH-
53	C_6H_5-CH=CH-CH=CH-

Fig. 1. Chemical structures of these photocrosslinkable polymers

3. SHG MEASUREMENT

The polymer films were poled by corona discharge in either wire-to-plane or needle-to-plane configuration. The detailed poling arrangement in wire-to-plane geometry was reported earlier.[7] In the needle-to-plane geometry, a sharp tungsten needle at a high voltage (5 KV) is positioned above the sample placed on a heated aluminum plate. This set-up was employed for *in situ* SHG measurements to study and control the poling and crosslinking process. It took about 15 minutes to heat the sample from room temperature to the poling temperature which was set at 5 ^{0}C below T_g. The sample was maintained at elevated temperature for 5 minutes and cooled down to room temperature by blowing air for about 5 minutes with the poling field on. Crosslinking was achieved by UV irradiation when the sample cooled down to room temperature but with the poling field maintained. A mercury lamp producing an intensity of 2 mW/cm^2 on the sample with emission peaked at 254 nm was utilized for polymers 40 and 43. A second mercury lamp emitting primarily at 366 nm with 8.5 mW/cm^2 intensity on the film surface was employed for polymers 50 and 53. The exposure time was chosen as 10 minutes for polymers 40 and 43. and 1 minute for polymers 50 and 53.

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Table I

Optical properties of these novel polymers

Polymer	40	43	50	53
Absorption peak λ (nm)	385	373		
n at λ (nm)				
532	1.638	1.696	1.664	1.711
633	1.635	1.680	1.627	1.656
1064	1.556	1.621	1.612	1.627
d_{33} (pm/V)	3.2	7.0	5.0	8.8
r_{33} (pm/V)	2.4	4.8	2.9	5.0

A Q-switched Nd:YAG laser of 10 ns pulse width with 15 mJ pulse energy at 1.064 µm was used for SHG measurements. The detailed SHG experimental set-up and calculations of the second-order NLO coefficient d_{33} have been reported elsewhere.[7-9] The measured d_{33} values of these polymer systems are summarized in Table I. The thermal relaxation behavior of SH intensity for one of the poled polymer (polymer 43) measured at room temperature is shown in Fig. 2. In the crosslinked state the second harmonic signal shows significant stability compared to the uncrosslinked polymer.
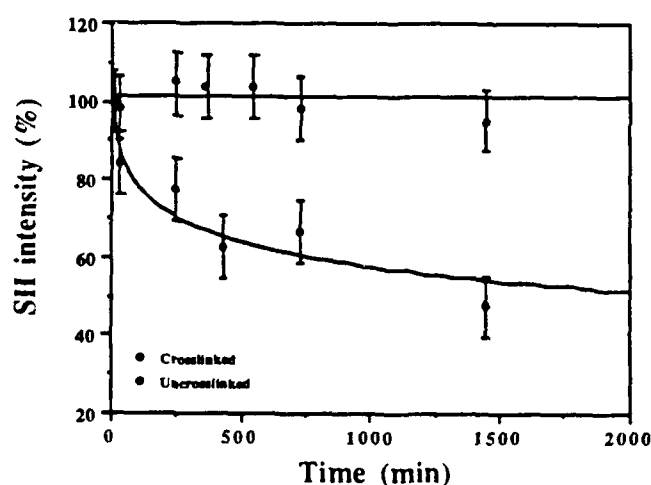

Fig. 2. Thermal relaxation behavior of SH intensity for polymer 43

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4. LINEAR ELECTRO-OPTIC COEFFICIENT MEASUREMENT

A modified Michelson interferometer was employed to measure the linear electro-optic coefficients of these polymer systems. The experimental arrangement of this interferometer is schematically shown in Fig. 3. A He-Ne laser (at 633 nm) beam is split into a sample beam and a reference beam. The sample beam propagates via the indium-tin-oxide (ITO) coated glass, the poled and crosslinked polymer film, and is then reflected back by a metal electrode. When this reflected sample beam is combined with the reflected reference beam, interference fringes are produced. An AC modulating field of amplitude of about 10 V and a frequency of a few kHz was applied across the polymer film. A photodetector with an adjustable slit and a lock-in amplifier were used to measure the modulations at two half-intensity points of a selected interference fringe at the modulating frequency ω, noted as I_ω^+ and I_ω^-. The linear electro-optic coefficient r_{13} is then given by:

$$r_{13} = (1 / 2\pi n^3) [(I_\omega^+ - I_\omega^-) / (I_{max} - I_{min})] (\lambda / V_m)$$

where n is the refractive index, λ is the laser wavelength, V_m is the modulating voltage, and I_{max} and I_{min} are the maximum and minimum intensities of the selected fringe respectively.
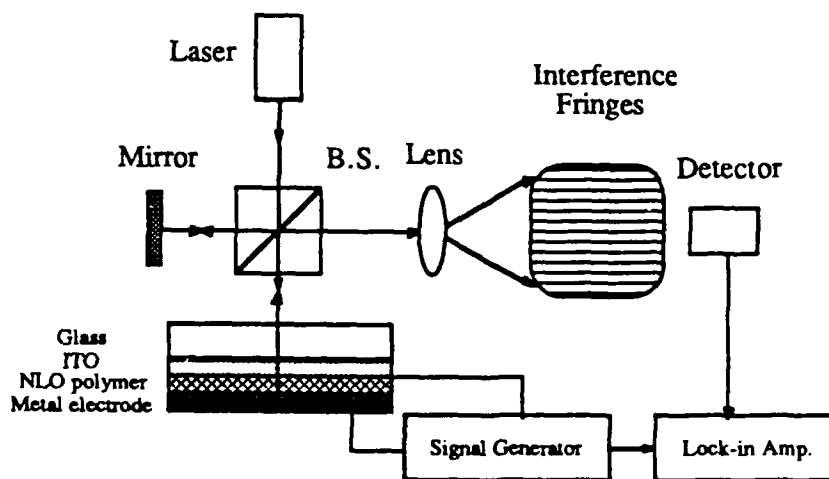

Fig. 3. Experimental arrangement of the modified Michelson interferometer

The measured linear electro-optic coefficients r_{33} of these polymers with this interferometer are also summarized in Table I, where $r_{33} = 3 r_{13}$ is assumed.

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5. CONCLUSIONS

The linear optical and second-order NLO properties of the novel polymer systems have been investigated. These polymer systems, when poled and sufficiently photocrosslinked, exhibit quite stable second-order optical nonlinearity at room temperature. The second-order NLO and the linear electro-optic coefficients were measured.

6. ACKNOWLEDGEMENT

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